

Electrochemical Surface Finishing

by E. J. Taylor and M. Inman

Electrochemical surface finishing is a highly scalable manufacturing process that traditionally uses viscous, non-aqueous and/or highly acidic electrolytes to achieve the desired surface profiles on metallic parts, with the addition of aggressive, hazardous chemical species to remove the oxide film on strongly passive materials. An emerging approach applies pulse and pulse reverse electric fields to control current distribution, mitigate oxide film formation and achieve the desired surface finish, in the presence of environmentally benign and simple chemistries. This approach lowers the cost of the manufacturing process, and improves process robustness. After a brief discussion of electrochemical surface finishing processes, case studies that describe deburring of automotive gears and electropolishing of semiconductor valves and superconducting radio frequency cavities are presented in this article.

Conventional Electrochemical Surface Finishing Processes

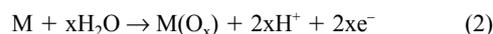
Electrochemical surface finishing removes metal in a selective manner from the surface of the workpiece by converting the metal into ions by means of an applied electric field. This is accomplished in an electrolytic cell by applying a positive (anodic) potential to the workpiece and a negative (cathode) potential to the tool used to shape the workpiece. While fundamental investigations of electrochemical metal removal processes typically employ a 3-electrode system, a manufacturing environment is typically not conducive to the use of reference electrodes. Therefore, most electrochemical manufacturing systems are based on a two-electrode cell.

Conventional electrochemical surface finishing relies heavily on the “art” of chemical mediation for process control. Under the influence of a constant electric field and controlled electrolyte flow, aggressive chemical species diffuse to the electrochemical interface and control the preferential dissolution of asperities from a surface via an electrolytic reaction, which may be generally represented as:



The selection of the appropriate electrolyte is, in part, dependent upon the initial surface finish. Landolt defined large asperities as features greater than $\sim 1 \mu\text{m}$,¹ for which low conductivity electrolytes are used to affect a primary current distribution, such that the voltage gradient between the asperities and the recesses of the surface is magnified, and the asperities are preferentially removed. These low conductivity electrolytes are generally used for applications such as deburring.^{2,3} For asperities smaller than $\sim 1 \mu\text{m}$,¹ high viscosity electrolytes are used to affect a tertiary current distribution such that under mass transport control, the limiting currents are higher at the tip of asperities than in the recesses and the asperities are again preferentially removed. Jacquet⁴ was one of the first to report that the optimum region for electropolishing is the mass transport or current limited plateau in the polarization curve based on a viscous salt film model.

Furthermore, during anodic metal dissolution (Eq. 1) some metal surfaces can form a passive oxide film, generally described as:



For strongly passivating metals, continued electropolishing under direct current (DC) electric fields in a simple electrolyte can lead to a roughened surface similar to pitting corrosion. Aggressive chemicals are therefore added to the electrolyte to remove the passive film

to enable uniform polishing. For example, hydrofluoric acid and/or fluoride salts are added to traditional electrolytes to depassivate the surface for strongly passive metals such as niobium and Nitinol alloys.⁵ In addition to the electrolyte handling and safety issues associated with concentrated hydrofluoric acid, conventional DC electropolishing of these materials presents process control issues, and reject rates can be as high as 40 to 50%.⁶

This reliance on chemical mediation can be traced back 150 years when the understanding of electrochemical principles was nascent. The history of electrochemical processing is full of stories regarding the serendipitous “discovery” of chemical components of electrolytes leading to the desired surface properties and profiles. These discoveries ultimately became the paradigm for development of new electrolyte chemistries, which led to the proprietary chemical additives of today’s chemical suppliers. This chemical mediation paradigm has the undesirable side effects of environmental waste and worker safety concerns, poor process control, and process performance limitations. Consequently, electrochemical surface finishing electrolytes are typically complex and difficult to control, and environmentally unfriendly.

Shifting the Paradigm to Pulse/Pulse Reverse Surface Finishing Processes

An emerging approach shifts the paradigm from the art of chemical mediation to the science of electrochemical kinetics and mass transport phenomena. Rather than relying on the diffusion of aggressive chemical species to the electrochemical interface, and on the continual need for maintenance of key chemical species in the electrolyte, user-defined asymmetric pulsed electric fields are utilized to directly control the interfacial process.

Figure 1 includes a schematic of an electropolishing process setup and a generalized electropolishing pulse reverse waveform for electropolishing of a niobium superconducting radio frequency cavity, as discussed below. A pulse reverse waveform for electrochemical metal removal begins with an anodic pulse that is tuned (on-time, t_a , and peak voltage, V_a) to enhance mass transport and control current distribution. While a priori determination of the on-times and peak voltages is difficult, guiding principles based on single pulse transient studies have been presented.⁷ Generally speaking, for uniform polishing of a surface, for hydrodynamic boundary layers conforming to the roughness features (*i.e.*, a macroprofile), the anodic on-time should be relatively small. For hydrodynamic boundary layers much larger than the roughness features (*i.e.*, a microprofile), the anodic on-time should be relatively large. Furthermore, for oxide forming or passive materials, anodic-only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film.^{8,9}

To depassivate the surface, cathodic pulses (on-time, t_c , and peak voltage, V_c) are interspersed within the anodic pulses, in place of or in conjunction with off-times, t_{off} .¹⁰⁻¹³ The off-times are generally inserted between the anodic and cathodic pulses to facilitate replenishment of reacting species and removal of by-products and heat. The cathodic pulse eliminates the need for aggressive chemical species such as HF and/or fluoride salts to remove the surface oxide. While the exact mechanism of depassivation is unknown at this stage, we speculate that the cathodic pulses remove the oxide film either by direct electrochemical reduction or indirect chemical reduction, and restore the virgin metal surface prior to the next anodic pulse. The amplitude of the cathodic pulses required for depassivation is material specific, and appears to be based on the free energy of formation of the passive film.

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Some have suggested using non-aqueous or low water content electrolytes to remove the source of oxygen leading to the formation of the passive film.¹⁴⁻¹⁶ However, from an industrial perspective, these processes are difficult to implement and control, due to several factors such as the hygroscopic nature of some non-aqueous electrolytes, issues with solubility and conductivity and with issues related to toxicity.

The inclusion of cathodic pulses and off-times in the waveform suggests that the overall process would be much slower than a conventional DC process, which is undesirable for industrial implementation. However, the maximum instantaneous current density available during the anodic pulse is higher than the DC limiting current density. Specifically, the ratio between the limiting current density realized in the pulsed electropolishing process, i_p , versus that in steady state, i_{lim} , is:

$$i_p / i_{lim} = [\delta_p / \delta (1 - \gamma_a) + \gamma_a]^{-1} \quad (3)$$

where δ_p is the pulsating diffusion layer thickness, δ is the steady state (DC) boundary layer thickness, and γ_a is the anodic duty cycle, or the ratio of the anodic pulse to the total period of the waveform. Ibl and colleagues¹⁷⁻¹⁹ discussed a “duplex diffusion layer” consisting of an inner pulsating layer and an outer stationary layer. Modeling work by Landolt also suggested the existence of a pulsating diffusion layer.²⁰ By assuming a linear concentration gradient across the pulsating diffusion layer and conducting a mass balance, Ibl derived the pulsating diffusion layer thickness (δ_p) as:¹⁸

$$\delta_p = (2Dt_{on})^{1/2} \quad (4)$$

where D is the diffusion coefficient and t_{on} is the pulse length. When the pulse on time is equal to the transition time (τ), the concentration of reacting species at the interface drops to zero precisely at the end of the pulse. An expression for τ is provided in the following equation:

$$\tau = ((nF)^2 C_b^2 D) / 2i_p^2 \quad (5)$$

where n is the number of electrons, F is the Faraday constant and C_b is bulk concentration. More exact solutions are given by integrating Fick's diffusion equation:

$$\delta_p = 2((Dt_{on}) / \pi)^{1/2} \quad (6)$$

$$\tau = \pi((nF)^2 C_b^2 D) / 4i_p^2 \quad (7)$$

More recently, Yin²¹ using a similar approach as Ibl, derived the same equation for the pulsating diffusion layer for “pulse-with-reverse” electrochemical processes.

Per Eq. 3, because δ_p must be smaller than δ , higher instantaneous limiting current densities can be achieved in pulsed processes. The extent of this increase is based on the δ_p / δ ratio, which is directly influenced by the anodic pulse on time. A higher instantaneous limiting current density relates directly to a higher instantaneous metal

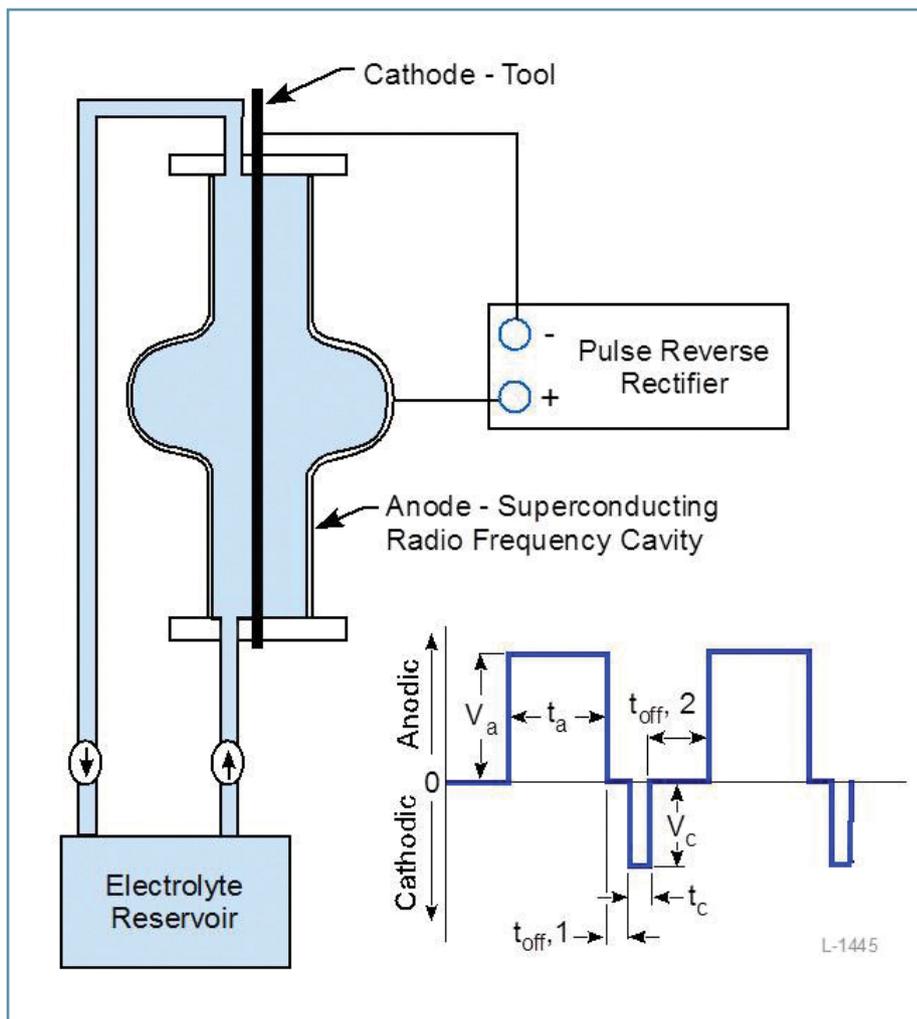


Fig. 1. Schematic of the electrochemical setup and pulse reverse waveform for electropolishing of a niobium superconducting radio frequency cavity.

removal rate. Therefore, the overall removal rate of a pulsed process can rival or exceed that of a DC process despite a duty cycle that is less than 100%. The waveform is designed such that the anodic pulse compensates for off-times and cathodic pulses such that the average material removal rate (net anodic current density) is equivalent to or greater than DC electropolishing. While rates are material and part geometry specific, as discussed herein the material removal rate for a stainless steel valve using a pulse reverse process was more than three times greater than that for the baseline DC process.

In summary, while conventional electropolishing uses a high viscosity electrolyte to focus the current distribution under mass transport, and aggressive chemicals to remove the oxide film, pulse reverse electropolishing is based on non-viscous, environmentally benign, simple chemistries and 1) uses the anodic pulse time and amplitude to focus the current distribution by qualitatively considering the effects of anodic pulse on-time to pulsating boundary layer thickness and the pulse amplitude on the transition time, 2) uses a cathodic pulse to remove the oxide film, and 3) uses an off-time to dissipate heat and reaction byproducts. As described above, there is some theoretical guidance as to the design of the waveform for a particular application. However, the fundamental understanding of the effects of pulse reverse waveforms on electrochemical processes has not yet been sufficiently developed to readily identify the required parameters without some experimentation. It is far more complex to model a dynamic train of anodic and cathodic pulses than a constant electric field. However, the lack of a predictive model does not, and should not preclude us from utilizing the advantages of pulse reverse electric fields in manufacturing applications.

Pulse reverse processes retain the advantages of high speed and low capital investment common to many electrochemical engineering manufacturing solutions. Herein, we discuss case studies detailing the use of pulse (anodic only) electrochemical deburring of steel automotive planetary gears, pulse reverse electropolishing of stainless steel semiconductor valves in aqueous sodium chloride/sodium nitrate, and pulse reverse electropolishing of pure niobium superconducting radio frequency (SRF) cavities used for high energy particle physics accelerators.

Electrochemical Surface Finishing Case Studies

Electrochemical Deburring of a Carbon Steel Planetary Gear for Ford Motor Co.

Traditional approach.—Removing rough edges and burrs from manufactured parts is an important industrial challenge. Deburring is often accomplished with manual labor using rudimentary tools and implements. Issues in terms of cost, quality, and worker repetitive motion injury are concerns with manual deburring operations. Ford Motor Co. sought a reproducible cost-competitive process to replace their current manual deburring activities.³ The part of interest (Fig. 2) was a cast iron (SAE 1010 steel) planetary carrier with oil grooves that had burrs from the milling processes. Initially, Ford engineers worked on an electrochemical deburring process based on an electrolyte of ethylene glycol, ammonium salt, nitric acid and a small amount of water. During initial production trials (~8,000 parts), several problems were noticed: 1) limited tool (cathode) lifetime, 2) worker and plant exposure to ammonia odor, and 3) high electrolyte cost and maintenance. Specifically, daily additions of nitric acid and water were required to maintain the pH between 5 and 6, and the electrolyte replacement cost was ~\$20,000.

Emerging approach.—The development of a pulsed electrochemical deburring process using an aqueous NaCl/NaNO₃ (~15 % wt) electrolyte was explored. Since 1010 steel is not a strongly passivating material, cathodic pulses were not required, and short anodic pulses were utilized to focus the current field on the burrs. The process was incorporated into an automated machine that enabled a processing time of 45 seconds, leading to a through-put of ~300 parts per hour. The process, which has been in operation since 1997, does not require active chilling and only needs a twice monthly addition of makeup water. The NaCl/NaNO₃ solution is replaced every 6 months to remove oils and contaminant buildup from drag-in, and the cost of electrolyte replacement is a fraction of the cost of the ethylene glycol-based electrolyte. The electrochemical deburring leads to iron hydroxide particles which are removed by a magnetic separator and Ford engineers report excellent tool life and process robustness.³ Finally, we estimate that almost \$400,000 could have been saved in the capital cost of the machine, if the machine had originally been designed for the NaCl/NaNO₃ process, instead of the ethylene glycol/ammonium salt-based process. Figure 2 provides an example of the efficacy of this process.

Electropolishing Valves for Swagelok Corp.

Traditional approach.—Stainless steel (300 Series) valves, fittings and tubular products are used for semiconductor process fluid control and delivery. The internal surfaces of these valves must be polished to a mirror-like finish. Previous practice for achieving said finish involved a two-step process, 1) abrasive flow machining (AFM) for deburring and bulk material removal of the tool lines, followed by 2) conventional electropolishing to achieve the final mirror-like surface finish. The electropolishing process used a chilled electrolyte solution consisting of a low conductivity and viscous concentrated sulfuric/phosphoric acid as well as proprietary additives. The AFM media was expensive and the combined AFM/electropolishing process difficult to control.

Emerging approach.—The development of a pulse reverse electrolytic process for both bulk material removal and electropolishing based on pulse/pulse reverse waveforms in an aqueous NaCl/NaNO₃ (~15 % wt) electrolyte was explored. The same electrochemical cell used for the conventional electropolishing process was used here, so no additional capital outlay was required. Due to the requirement

for both bulk removal and final electropolishing, we developed a two-step sequenced waveform¹³ which polished the surface from a “roughness average” (R_a) surface finish of approximately 1 μm to a mirror-like finish with a final R_a of 0.026 μm after 45 seconds. This is in comparison to the prior process that took ~3 minutes for the electropolishing step alone. Note, R_a is a commonly used measurement of surface roughness based on the arithmetic average of the absolute values of the surface peaks and valleys. Figure 3 shows an example of a SS316 tubular part electropolished using the pulse reverse process.

Electropolishing of Nb Superconducting Radio Frequency Cavities

Traditional approach.—Niobium is used to fabricate Superconducting Radio Frequency (SRF) cavities used for high-energy particle physics accelerators, such as the International Linear Collider. To take full advantage of the superconducting properties of the niobium SRF cavities, the interior surface must be electropolished to a microscale roughness. Conventional DC electropolishing of niobium is conducted in a viscous electrolyte consisting of nine parts sulfuric acid (96%) to one part hydrofluoric acid (48%).⁵ This electrolyte is an extreme hazard to workers and requires costly safety protocols with expensive waste treatment costs. Furthermore, the viscous electrolyte necessitates the use of a horizontally rotating

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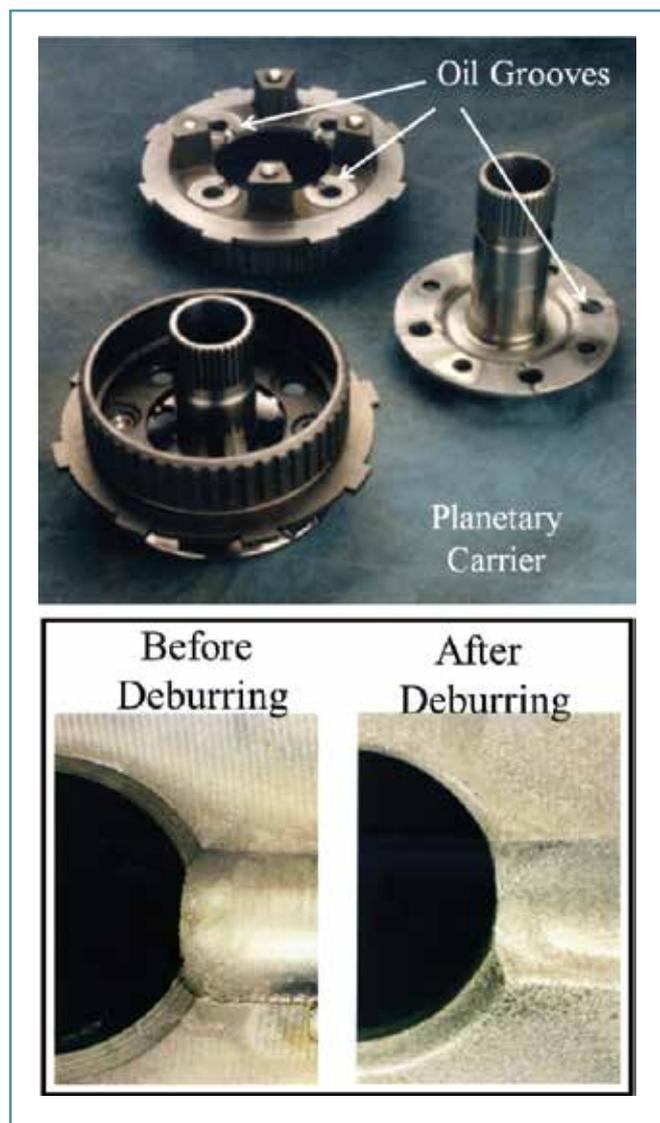


FIG. 2. SAE 1010 planetary gear (top) before (left) and after (right) pulse deburring in a NaCl-NaNO₃ electrolyte.

cavity, 60% filled with electrolyte, to enable the escape of hydrogen gas from the salt film at the surface. This requires elaborate sealing equipment, and limits the industrial implementation at large part volumes.

Emerging approach.—The development of a pulse reverse process to electropolish pure Nb SRF cavities in an electrolyte of 5-10 wt% sulfuric acid in water was explored. It is speculated that the process works indirectly, wherein an oxide film is first formed during the anodic cycle and subsequently removed during the cathodic cycle to effectively consume niobium metal, rather than direct electrochemical

oxidation of Nb to Nb²⁺ in solution.²² This mechanism is termed “cathodic electropolishing,” and while it may be applicable to other materials, is a phenomenon that to date has only been observed with electropolishing of strongly passivating materials such as pure niobium.

In bench-scale feasibility experiments, flat 25 x 25 mm niobium coupons were processed in aqueous H₂SO₄ electrolytes and a variety of pulse reverse waveform parameters were explored. The desired surface finish (< 0.05 μm measured using a Mitutoyo SJ-400 stylus profilometer, at the minimum detection limit of this measurement tool) and level of cleanliness, comparable to that obtained using standard electropolishing (9 parts H₂SO₄ (96%) to 1 part HF (49%)) was achieved.²³

While this demonstration was impressive at the bench-scale, the true value to the high-energy physics community could only be realized by scaling up the niobium electropolishing process to single-cell and nine-cell SRF cavities. To facilitate this technology transition, the process was first investigated on larger flat coupons, 75 x 75 mm square, to optimize current density scaling factors, edge effects and the anode-cathode gap. The SRF cavities have varying anode-cathode gap, ranging from ~1 to 3.4 inches, which affects the uniformity of the applied current, and therefore the polishing uniformity throughout the cavity. This potential non-uniformity can be alleviated through specialized cathode design and waveform parameter selection.

In the final phase of the work to date, the knowledge gained in the flat coupon work was applied to implement the technology on single-cell cavities.²⁴ The electropolished cavities (Fig. 4) were evaluated at Fermilab and reported to achieve equivalent or better RF performance compared to traditional processing. Specifically, the maximum gradient reported in a single cell cavity was ~45MV/m with a Q of 1 x 10¹⁰, the highest gradient and Q value at this gradient observed at Fermilab in any cavity regardless of processing technique!²⁵

In contrast to traditional electropolishing, Fermilab also noted that if the pulse reverse process was implemented to electropolish Nb cavities, safety and environmental overheads would be reduced to a bare minimum. Furthermore, as this electrolyte does not seem to engender a viscous salt film on the surface, the cavity can be held in a vertical orientation and does not require rotation. This will enable industrial scale manufacturing in a simple manifold arrangement to process multiple cavities simultaneously at low cost.

Conclusions

Electrochemical engineering processes have long been applied to metal removal applications, such as electropolishing, deburring, and radiusing. However, due to the mechanistic aspects of conventional DC surface finishing, toxic and difficult-to-control chemistries are often required to obtain the desired surface finish and part dimension.



Fig. 3. 316SS fitting surface before (top) and after (bottom) pulse reverse electropolishing in an NaCl-NaNO₃ electrolyte.

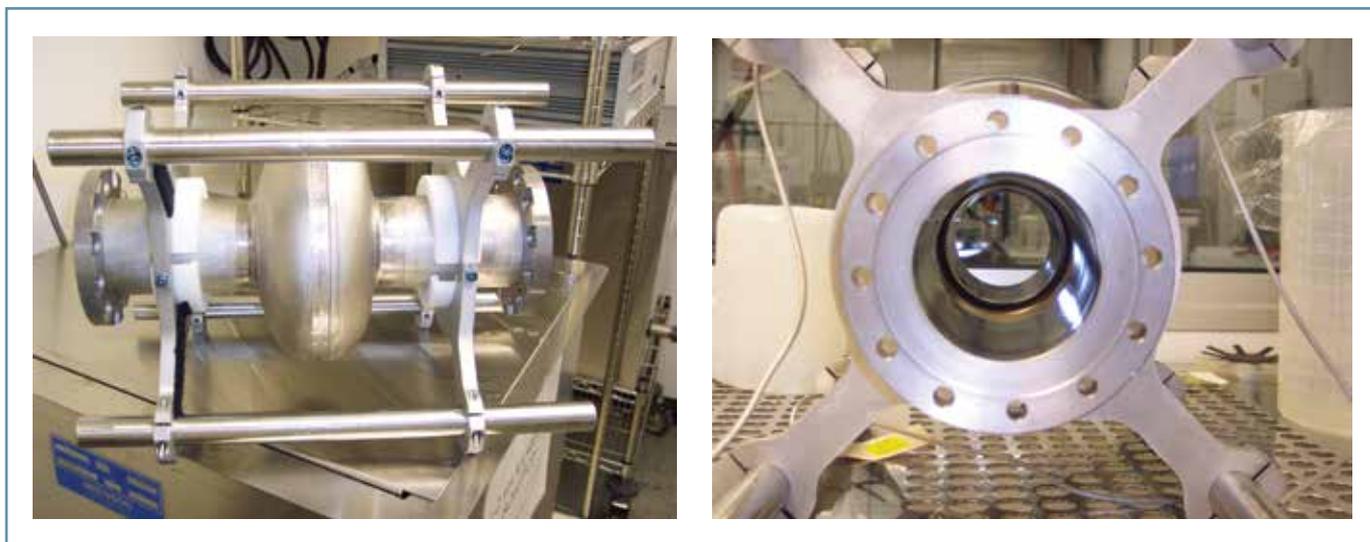


Fig. 4. (Left) Single-cell cavity in frame for electropolishing, (Right) Interior, electropolished surface.

Pulse or pulse reverse processes, by comparison, employ aqueous electrolytes that do not require specialized maintenance procedures, and do not require aggressive chemicals for depassivating the surface. Consequently, the safety and chemical handling and disposal issues associated with the pulse or pulse reverse surface finishing process are minimized, and costs are lowered and robustness is improved.

While the mechanistic aspects of the pulse and pulse reverse surface finishing processes are not fully understood, they are clearly distinct to those of conventional electrochemical surface finishing. However, this lack of fundamental understanding should not be a barrier to implementation at an industrial level, if there are cost and performance advantages conferred by pulse or pulse reverse processes. More insight into the mechanistic aspects of pulse/pulse reverse surface finishing processes is likely possible with three electrode studies, conducted in university or industrial research laboratories. This is an important and emerging area of electrochemical manufacturing engineering, and the results obtained in industry should encourage subsequent fundamental research to bring more mechanistic understanding. ■

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